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Cobalt(II), nickel(II) and zinc(II) coordination compounds derived from aromatic amines

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Co^{2+}
Ni^{2+}
Zn^{2+}

ABSTRACT

The structural and spectroscopic characterization of coordination compounds of four aromatic amines derived from benzimidazole, 2-aminobenzimidazole (**L1**), 1-(S-methylcarbodithioate)-2-aminobenzimidazole (**L2**), 2-(2-aminophenyl)-1H-benzimidazole (**L3**) and 6,6-dimethyl-5H-benzimidazolyl[1,2-c]quinazoline (**L4**) are reported. Cobalt(II) $[Co(L1)_2(CH_3COO)_2]$ (**1**) and nickel(II) $[Ni(L1)_2(CH_3COO)_2]$ (**2**) acetate coordination compounds of **L1** are discussed. The synthesis and the X-ray crystal structure of the new 1-(S-methylcarbodithioate)-2-aminobenzimidazole (**L2**) is informed, together with its cobalt(II) $[Co(L2)_2Cl_2]$ (**3**), $[Co(L2)_2Br_2]$ (**4**) and zinc(II) $[Co(L2)_2Cl_2]$ (**5**), $[Zn(L2)_2Br_2]$ (**6**) coordination compounds. In these compounds the imidazolic nitrogen is coordinated to the metal center, while the $ArNH_2$ and the S-methylcarbodithioate groups do not participate as coordination sites. A co-crystal of **L1** and **L2** is analyzed. Structural analyses of the coordination compounds of **L3** showed that this ligand behaves as a bidentate ligand through the aniline and the imidazole groups forming six membered rings in the cobalt(II) $[Co(L3)Cl_2]$ (**7**) and zinc(II) $[Zn(L3)Cl_2]$ (**8**) compounds, as well as the nickel(II) nitrate $[Ni(L3)_2(H_2O)_2](NO_3)_2$ (**9**). The quinazoline **L4** was produced by insertion of one acetone molecule and water elimination in **L3**, its X-ray crystal diffraction analysis, as well as that of its zinc(II) coordination compound $[Zn(L4)_2Cl_2]$ (**10**), are discussed.

1. Introduction

Continuing with our research on the coordination behavior of aromatic amines, we have analyzed the reactions of transition metal salts with four aromatic heterocycles: 2-aminobenzimidazole (**L1**), 1-(S-methylcarbodithioate)-2-aminobenzimidazole (**L2**), 2-(2-aminophenyl)-1H-benzimidazole (**L3**) and 6,6-dimethyl-5H-benzimidazolyl[1,2-c]quinazoline (**L4**), Scheme 1. These compounds contain benzimidazole and Ar—NH_2, Ar—NH or N—CS_2CH_3 groups. While imidazole is a strong Lewis base, Ar—NH_2, Ar—NH and N—CS_2CH_3 [1] are weak bases. No strong coordination to metal atoms is expected for weak bases except if the assistance of a second donor is present as in the case of **L2** and **L3** [2–6]. In **L1** the NH_2 in α position may also coordinate to the metal ion allowing the ligand to behave as bidentate forming a four membered ring [1,7], whereas in **L4** a monodentate coordination mode is only possible. Due to the different coordination modes expected for **L1**–**L4** and the wide variety of possible products, the present investigation was undertaken.

In our experience, the functionalization of benzimidazole with sulfur groups yields versatile ligands as bis[2-(1*H*-benzimidazol-2-yl)phenyl]disulfide [bis(2phSbz)], which can coordinate to metal centers by the imidazole and/or the sulfur atoms [8]. In its reactions with chlorides and bromides of Co^{2+}, Zn^{2+} and Cd^{2+}, the S—S bond was maintained and gave similar 11 membered chelate compounds. However, the reaction with $Ni(NO_3)_2$ caused the S—S bond cleavage giving the 2-(1*H*-benzimidazol-2-yl)thiophenyl coordination compound $[Ni(2phSbz)_2]$.

Previous results have shown that 1-methyl-2-dimethyldithiocarbonimidate-benzimidazole can be obtained from reaction of 1-methyl-2-aminobenzimidazole with KOH, CS_2 and CH_3I [9]. A similar reaction with 2-aminobenzimidazole gave the new polydentate ligand (**L2**) having the S-methylcarbodithioate moiety at N1—H.

The 2-(2-aminophenyl)-1H-benzimidazole (**L3**) may behave as a bidentate ligand through its aniline group assisted by the imidazole nitrogen. In the free ligand a strong hydrogen bond indicates the natural site for metal ion coordination [10], as confirmed by a boron coordination compound [11]. As we will discuss later on,

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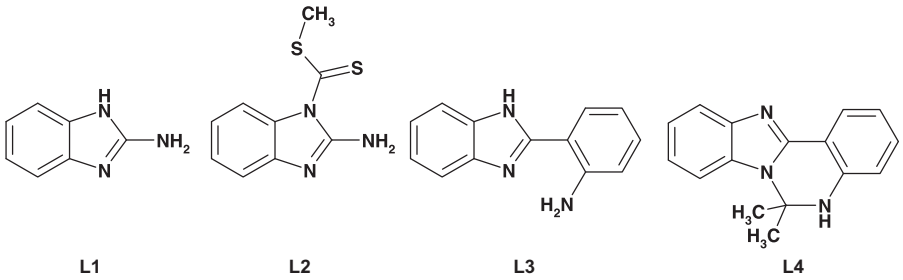

Scheme 1. Amine aromatic heterocycles.

reaction of **L3** with acetone afforded compound **L4** by water elimination, which is also a suitable ligand for metal ions.

2. Experimental

2.1. Physical measurements

FT IR spectra were recorded on a (Perkin–Elmer 1600) spectrophotometer using KBr pellets (4000–400 cm^{-1}). The UV–Vis–NIR spectra (diffuse reflectance, 40000–4000 cm^{-1}) were obtained on a Cary-5E (Varian) spectrophotometer. High resolution mass spectra were acquired by LC/MSD TOF on an Agilent Technologies instrument with APCI as ionization source. Melting points were measured on a Mel-Temp II apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker instrument. Elemental analyses were performed on Flash 1112 Thermo Finnigan.

2.2. Materials

The metal salts $CoCl_2{\cdot}6H_2O$, $CoBr_2$, $ZnCl_2$, $ZnBr_2$, $Co(CH_3COO)_2{\cdot}4H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and EtOH (J.T. Baker) were used without further purification. Ligand **L1** was acquired from Aldrich Co.

2.3. Synthesis

2.3.1. 1-(S-methylcarbodithioate)-2-aminobenzimidazole (*L2*)

To a solution of **L1** (10 g, 75 mmol) in DMF (20 mL), KOH pellets (4.63 g, 75 mmol) were added. The suspension was stirred for 2 h, then cooled in an ice bath and CS_2 (9 mL, 150 mmol) was added, followed by the addition of CH_3I (4.67 mL, 75 mmol), 2 h later. The mixture was stirred for 2 h. The reaction mixture was poured into water (1 L) and the precipitate filtered. A yellow solid was isolated (14 g, 84% yield). Mp 121 °C. Recrystallization from DMSO (100 mg in 0.4 mL), or from $CHCl_3$ (200 mg in 20 mL) after 2 weeks, afforded yellow crystals. NMR (DMSO-d_6, 27 °C, δ ppm) ^{1}H: 7.22 (H4), 7.12 (H5), 6.97 (H6), 7.73 (H7), 7.25 (NH2), 2.82 (CH_3). ^{13}C: 153.3 (C2), 116.3 (C4), 124.5 (C5), 120.3 (C6), 112.8 (C7), 132.8 (C8), 143.1 (C9), 205.0 (C=S), 21.5 (CH_3). ^{15}N: −202.3 (N1), −185.6 (N3), −315.3 (NH_2). *Anal.* Calc. for $C_9H_9N_3S_2$: C, 48.41; H, 4.06; N, 18.82; S, 28.72. Found: C, 48.58; H, 4.16; N, 18.74; S, 28.57%. TOF calc. for $[(C_9H_9N_3S_2{+}H)^+]$: 224.0310. Found: 224.0313. MS: *m*/*z* (%): 223(83) $[M]^+$. IR (KBr, *v* cm^{-1}): 3354, 1655, 1594, 1469, 1288, 742.

2.3.2. Co-crystal of 2-aminobenzimidazole and 1-(S-methylcarbodithioate)-2-aminobenzimidazole (*L1–L2*)

Crystallization of a solution of the mixture of **L1** (120 mg, 0.90 mmol) and **L2** (200 mg, 0.90 mmol) in MeOH/acetone (30 mL) afforded a co-crystal of both ligands. Mp 252 °C. *Anal.* Calc. for $C_9H_9N_3S2{\cdot}C_7H_7N_3$: C, 53.91; H, 4.52; N, 23.58. Found: C, 53.91; H, 4.81; N, 23.79%.

2.3.3. 2-(2-Aminophenyl)-1H-benzimidazole (*L3*)

The ligand **L3** was synthesized as previously reported [10], using a mixture of anthranilic acid (5 g, 36.5 mmol), *o*-phenylendiamine (3.9 g, 36.5 mmol) and polyphosphoric acid (50 g, 510 mmol). It was purified by crystallization from EtOH and brown–red crystals were obtained (4.96 g, 65%). Mp 211 °C. MS: *m*/*z* (%): 209(100) $[M]^+$, 194(1.0) $[M–NH]^+$. *Anal.* Calc. for $C_{13}H_{11}N_3$: C, 74.62; H, 5.30; N, 20.08. Found: C, 74.57; H, 5.70; N, 19.90%. IR (KBr, *v* cm^{-1}): 3464, 3319, 2950, 1594, 1521, 1428, 1164, 1129, 787.

2.3.4. 6,6-Dimethyl-5H-benzimidazolyl[1,2-c]quinazoline (*L4*)

The ligand **L3** (1 g, 4.78 mmol) was dissolved in acetone (10 mL) and the solution was slowly evaporated at rt. Light brown crystals were obtained after 4 days (1 g, 84%). Mp 253 °C. NMR (DMSO-d_6, 27 °C, δ ppm) ^{1}H: 7.72 (H4), 7.25 (H5, H6), 7.65 (H7), 6.83 (H12), 7.19 (H13), 6.80 (H14), 7.93 (H15), 6.94 (NH), 1.84 ($2CH_3$). ^{13}C: 147.0 (C2), 111.8 (C4), 121.8 (C5), 122.0 (C6), 118.8 (C7), 111.5 (C10), 142.9 (C11), 114.5 (C12), 131.5 (C13), 117.9 (C14), 124.6 (C15), 71.8 (C17), 27.9 ($2CH_3$). ^{15}N: −291.0 (N16) [$^{1}J(^{15}N, ^{1}H)$ = 86.9 Hz]. MS: *m*/*z* (%): 249(22) $[M]^+$, 234(100) $[M–CH_3]^+$, 209(1) $[M–2CH_3]^+$, 207(2) $[M–C(CH_3)_2]^+$, 194(5) $[M–NC(CH_3)_2]^+$. *Anal.* Calc. for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 76.68; H, 5.83; N, 17.14%.

2.3.5. [Co(L1)$_2$(CH$_3$COO)$_2$] (*1*)

The ligand **L1** (67 mg, 0.5 mmol) was dissolved in EtOH (10 mL) and a solution of $Co(CH_3COO)_2{\cdot}4H_2O$ (125 mg, 0.5 mmol) in EtOH (10 mL) was slowly added, then it was heated up to the boiling point for 10 min. The solution was let to stand at rt for 1 week and purple crystals were obtained. *Anal.* Calc. for $(C_7H_7N_3)_2Co(CH_3COO)_2$: C, 48.77 H, 4.55; N, 18.96. Found: C, 48.30; H, 4.51; N, 18.64%. IR (KBr, *v* cm^{-1}): 3410, 1646, 1562, 1274. μ_{eff} = 4.63 BM at 22 °C. UV–Vis–NIR (cm^{-1}): ν_2 = 8200 and ν_3 = 18300.

2.3.6. [Ni(L1)$_2$(CH$_3$COO)$_2$] (*2*)

The ligand **L1** (67 mg, 0.5 mmol) was dissolved in EtOH (10 mL) and a solution of $Ni(CH_3COO)_2{\cdot}4H_2O$ (124 mg, 0.5 mmol) in EtOH (10 mL) was slowly added, then it was refluxed for 24 h. After 5 days, a green precipitate was obtained. It was recrystallized by the diffusion method, with a solution of compound (50 mg) in EtOH (3 mL) and a mixture of EtOH/acetone (1:6). After 3 days green crystals were obtained. *Anal.* Calc. for $(C_7H_7N_3)_2Ni(CH_3COO)_2$: C, 48.79; H, 4.55; N, 18.97. Found: C, 48.57; H, 5.01; N, 18.63%. IR (KBr, *v* cm^{-1}): 3454, 1640, 1578, 1273. μ_{eff} = 3.15 BM at 22 °C. UV–Vis–NIR (cm^{-1}): ν_1 = 7960, ν_2 = 14900 and ν_3 = 24350.